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(54) PROCESS FOR CATALYTIC REFORMING OF NAPHTHA

VERFAHREN ZUR KATALYTISCHEN REFORMIERUNG VON NAPHTA

PROCEDE DE REFORMAGE CATALYTIQUE DU NAPHTHA

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Description

The present invention relates to a process for the catalytic reforming of naphtha.

Background

Catalytic reforming, or hydroforming, is a well established industrial process employed by the petroleum industry for improving the octane quality of naphthas or straight-run gasolines. In reforming, a multifunctional catalyst is employed which contains a metal hydrogenation-dehydrogenation (hydrogen transfer) component, or components, substantially atomically dispersed upon the surface of a porous, inorganic oxide support, notably alumina. Platinum metal catalysts, or platinum to which one or more additional metal promoters has or have been added to form polymetallic catalysts are currently employed, reforming being defined as the total effect of the molecular changes, or hydrocarbon reactions, produced by dehydrogenation of cyclohexanes and dehydroisomerization of alkylcyclopentanes to yield aromatics; dehydrogenation of paraffins to yield olefins; dehydrocyclization of paraffins and olefins to yield aromatics isomerization of n-paraffins; isomerization of alkylcycloparaffins to yield cyclohexanes; isomerization of substituted aromatics; and hydrocracking of paraffins which produces gas, and inevitably, carbonaceous material, (or "coke"), the latter being deposited on the catalyst.

During the course of a reforming operation, the activity of the catalyst becomes reduced, due to factors which include the progressive deposition of coke on the catalyst. The reduction in catalyst activity is apparent as a reduction in the amount of reformed high-octane naphtha. The octane number of the product naphtha can be maintained by raising the temperature of contact between the naphtha and catalyst, but this expedient is limited by the temperatures at which there is an unacceptable level of risk of damage to equipment used for the reforming process. When the maximum desirable operating temperature has been reached, it is necessary to regenerate the activity of the catalyst in order to restore the operation of the reforming process to economically useful levels.

GB-A-1113547 describes a reforming unit comprising a variable number of on-oil reforming reactors producing high octane and lower octane reformates. At the start of the operation of the unit, n reactors are on-oil to produce high-octane reformate.

When the last on-oil reactor becomes deactivated, it is taken offstream and the unit operates with n-1 reactors to produce low-octane reformate. During this operating period, the off-stream reactor is regenerated. When the last of the n-1 reactors becomes deactivated, it is replaced by the regenerated off-stream reactor, so that low-octane reformate production is maintained during a second operating period with n-1 reactors. The off-stream reactor is regenerated during the second oper-

ating period and may subsequently be used as a substitute for the last of the on-stream n-1 reactors when deactivated. Upon the upstream reactors becoming deactivated, all n reactors are connected in series for regeneration, whereafter described cycle is repeated.

Regeneration processes in fixed-bed catalytic reforming operations are basically of two types. In a so-called semi-regenerative process, the entire unit is operated by gradually and progressively increasing the temperature to maintain the activity of the catalyst, (which activity is reduced by coke deposition) until finally the entire unit is shut down for regeneration, and reactivation, of the catalyst. After regeneration and reactivation of the catalyst, the unit is put back on-oil. In a cyclic regeneration process, the reactors are individually isolated, or in effect swung out of line by various manifold-
ing arrangements, motor operated valving and the like. The catalyst is regenerated to remove the coke deposits, and then reactivated while the other reactors of the series remain on stream. A "swing reactor" temporarily replaces a reactor which is removed from the series for regeneration and reactivation of the catalyst, until it is put back in series. The cyclic method of regeneration offers advantages over the semi-regenerative type process in that regenerative type process in that regeneration and reactivation of the catalyst is effected in the isolated reactor without shutting down the unit and there is no loss of production. Moreover, because of this advantage, the unit can be operated at higher severities (that is, lower pressures and higher temperatures) to produce higher C_6^+ liquid volume yields of high octane gasoline than semi-regenerative reforming units. However, reforming units adapted for cyclic operation are considerably more costly than units adapted for semi-regenerative operation, and the costs involved in converting a semi-regenerative unit for cyclic regeneration are prohibitively high.

Present semi-regenerative reforming units are usually operative to provide a reformate having an octane rating or octane number of less than 102 because the production of higher rated reformates accelerates catalyst deactivation and hence leads to unacceptably short periods of operation between shut-downs for regeneration. One way of dealing with the resulting reduced cycle-length time (i.e., the minimum time between similar phases of contiguous operations of the unit) is to increase the amount of catalyst in the reactors of the unit. Unfortunately such an expedient results in conversion of the naphtha feed to low value gases and reduces the yield of high octane naphtha.

It will be understood from the foregoing that there is a strong incentive to provide a means of modifying existing semi-regenerative reforming units so that they can produce high yields of high octane naphtha. The incentive is all the greater as legislation is enforced against the addition of octane-boosting lead compounds to naphtha.

The present invention provides catalytic reforming

process performed in a reforming unit operated with a constant plural number of on-stream catalyst-containing reaction zones connected in series, wherein feed naphtha is passed into the first (or upstream) reaction zone of the on-stream series of reaction zones in the unit and product naphtha having a higher octane rating than the feed naphtha is recovered from the last (or downstream) zone of the on-stream series of reaction zones in the unit, the process comprising, in sequence, the steps of:

(a) passing naphtha into and through the on-stream series of reaction zones of the unit and progressively increasing the temperature of at least the last zone of the on-stream series of zones to maintain the octane rating of the product naphtha at least at a given value until the last on-stream reaction zone of the series attains a specified maximum operating temperature corresponding with a specified degree of deactivation of the catalyst therein;

(b) substituting a different reaction zone containing active reforming catalyst in place of the previous said last on-stream reaction zone of the series in step (a) to maintain a constant number of series-connected reaction zones in the unit, the said previous last reaction zone being maintained off-stream;

(c) continuing the reforming process by passing feed naphtha through the on-stream series-connected reaction zones of the unit without regenerating/reactivating the catalyst in the said previous last reaction zone, and recovering a naphtha product having at least the given octane rating from the last on-stream reaction zone of the series;

(d) progressively raising the temperature of at least the last reaction zone of the said on-stream series of reaction zones to maintain at least the given octane rating of the product naphtha until the last on-stream reaction zone of the series attains a given maximum operating temperature;

(e) optionally repeating steps (b), (c) and (d), employing a different substitute reaction zone for each step (b);

(f) interrupting the passage of naphtha into and through all the series-connected reaction zones of the unit, and regenerating catalyst (by *in situ* and/or *ex situ* regeneration) during the interruption in all the reaction zones employed for reforming in steps (a) to (e); and

(g) optionally repeating steps (a) to (f).

The amount of catalyst in the last reactor of the series in the unit may comprise from 50 to 90 weight per-

cent of the total catalyst in the unit. The first reactor of the series in the unit may contain from 5 to 20 weight percent of the total catalyst in the unit.

In step (a), the temperature of the first reactor may be progressively raised to maintain the octane rating of the naphtha product.

The unit may comprise at least two, and usually three reactors connected in series.

In step (a), the temperature of other reactor(s) between the first and last reactors may be progressively raised to maintain the octane rating of the naphtha product.

The amount of catalyst contained in the reactors connected between the first and last reactors of the series may be in a range of from 5 to 45 weight percent of the total catalyst in the unit.

Step (f), may be effected by *in situ* regeneration and reactivation of catalyst in the reactors of the unit and at least one spare reactor, the spare reactor(s) being connected or connectable to form part of the unit for step (f).

Following the regeneration and reactivation, the spare reactor(s) may be disconnected from the unit, and step (a) may be started.

The present invention can be performed in a catalytic reforming unit for the catalytic reforming of naphtha comprising a plurality of catalyst-containing reactors connected in series for the passage of naphtha through the unit from the first reactor of the series to the last reactor thereof, means for heating naphtha passing from one reactor to the next reactor in the series, means for heating naphtha passing to the first reactor of the series, recovery means for recovering reformed naphtha from the last reactor of the series, a substitute catalyst-containing reactor (which may contain substantially the same amount of catalyst as the said last reactor), means for diverting naphtha to circulate from the last-but-one reactor of the series to the substitute reactor whereby the substitute reactor functions as the last reactor of the series.

The last reactor and the substitute reactor may be connected in parallel with each other to receive naphtha from the last-but-one reactor of the series and to discharge naphtha to the said recovery means, there being valves which may be operable to cause naphtha to pass through only one or other, at a time, of the said last reactor and the substitute reactor.

At least some of the said valves may be operable to cause catalyst regenerating/reactivating vapors to pass through the said last reactor and the said substitute reactor at the same time during a catalyst-regeneration/reactivation operation of the unit. Preferably, the regenerating/reactivating vapors pass through the last reactor and the substitute reactor in series.

The invention is now further described with reference to non-limitative embodiments thereof and with reference to the accompanying drawing. The embodiments are given by way of example and are not limitative of the scope of the invention.

The drawing is a simplified flow sheet of a reforming unit, and the drawing shows those features which are important for illustration of the principle of the process of the invention. Items of equipment which are not shown, but which would be appreciated by a person skilled in the art, have been omitted.

Referring to the drawing, feed naphtha from a storage facility 11 is passed via pipes 12 and 13 to a preheat furnace 14 wherein the temperature of the naphtha is raised to a suitable or conventional naphtha-reforming temperature. Catalytic reforming of naphtha is effected in the presence of hydrogen, and although hydrogen is often a by-product of reforming, it is preferred to add a hydrogen-containing gas to the naphtha feed passing to the reformer-reactors. A hydrogen-containing gas in a pipe 15 is circulated by a circulation fan 16 into pipe 13 so that the naphtha passes to the furnace 14 in admixture with hydrogen.

The preheated naphtha and hydrogen mixture is circulated from the furnace 14 via a conduit 17 to a first-stage reactor 18 containing a naphtha reforming catalyst, e.g., a catalyst comprising platinum dispersed on a halogen-containing alumina support and optionally containing promoter metals and other components, such as sulfur. The reforming reactions which occur in the first stage reactor 18 include the conversion of substituted and unsubstituted cyclo-paraffins to aromatics with the production of hydrogen and the isomerization of n-paraffins to iso-paraffins, inter alia. The aforesaid, and other reactions, are endothermic in sum, and the effluent stream leaving the reactor 18 is at a lower temperature than the stream entering the reactor 18.

The effluent stream from the first-stage reactor 18 is recovered in conduit 19 and passed via a re-heat furnace 20 into conduit 21 which conducts the reheated stream to a second-stage reactor 22. The re-heat furnace raises the temperature of the effluent stream from reactor 18 to a temperature suitable for the second-stage reforming reactions in the second-stage reactor 22.

The second-stage reactor 22 contains a naphtha reforming catalyst which may be the same as, or different to, the catalyst in the reactor 18. The second-stage reactor 22 operates at a temperature which is similar to or generally somewhat higher than the temperature in the first reactor 18. The principal naphtha-reforming reactions in the second-stage reactor 22 include the conversion of paraffins to aromatic hydrocarbons. The foregoing reactions are, in sum, endothermic and the effluent from the reactor 22 is at a lower temperature than the feed thereto.

The effluent from the second-stage reactor 22 is recovered in line 23 and passed through a reheat furnace 24 where it is heated to a temperature suitable for the naphtha reforming reactions in a third-stage reactor 25. Reheated effluent from the furnace 24 passes to the third-stage reactor 25 via line 26.

The third-stage reactor 25 contains a naphtha-re-

forming catalyst which may be similar to, or the same as, the catalyst in one or both of the other reactor stages, and the third stage reactor 25 is operated at a temperature which is similar to or slightly higher than the temperature in the second-stage reactor 22. The principal naphtha-reforming reactions in the third-stage reactor 25 include the conversion of paraffins to aromatics and low-molecular weight products and by-products.

The aforesaid reactions may, in toto, be either endothermic or exothermic.

The effluent from the third stage reactor 25 is recovered in line 27, and conducted via product line 28 and a cooler 29 to a separator 30. The cooler 29 condenses reformed naphtha liquids (e.g., C₄-hydrocarbons) so that reformed naphtha can be separated from the gases (H₂ and light hydrocarbons) formed during the reforming reactions. The cooler 29 may be a heat exchanger which serves to preheat feed naphtha passing via line 13 from line 12 with hydrogen-containing recycle gas from line 15.

Liquid reformate is recovered from the separator 30 via line 31, and the gases pass into line 32. At least some of the gases are circulated by the fan 16 (which may be optionally supplemented by another circulation fan 33, which could comprise an additional compression stage of fan 16) to line 15 for use in the reforming process as described. Excess gases are recovered in line 34 and stored and/or discharged in and/or from facility 35.

The amounts of reforming catalyst in the first, second and third stage reactors are usually different from each other. Typically, the first-stage reactor may contain from 5 to 12 w% (e.g., about 10 w%) of the total reforming catalyst in the three reforming stages; the second stage reactor may contain from 10 to 25 w% (e.g., about 20 w%) of the total catalyst, and the third-stage reactor may contain from 63 to 85 w% (e.g., about 70 w%) of the total catalyst. These different quantities of catalyst and the different operating temperatures of the reforming stages are to take account of the different types of reforming reactions which are significant in each stage.

During the course of a naphtha-reforming operation, a carbonaceous material, termed "coke", deposits progressively on the catalyst and reduces its activity. The amount of coke deposition is lowest in the first-stage reactor, highest in the third (or last) stage reactor, and intermediate in the second (or intermediate) stage reactor or reactors. Eventually, the amount of coke deposition, and corresponding reduction in catalyst activity, is such that it is economic to interrupt the reforming process to restore the reforming activity of the catalyst by a so-called 'regeneration' process.

When the amount of coke on the catalyst in the last reforming stage is in the range of from 10 to 50 w% or higher (relative to the weight of catalyst in the last reforming stage), it is usually considered economic to interrupt reforming and initiate catalyst regeneration operations. The catalyst in the first reforming stage (e.g., reactor 18) would typically have a coke content in the

range of up to 5 w%, relative to the weight of catalyst in the first stage, and the coke content of catalyst in the intermediate stage (e.g., reactor 22) would typically be in the range of from 10 to 25 w%. The coke levels in the first and intermediate reforming stages are not so high as to reduce the reforming capability of the catalyst in the first and intermediate stages to uneconomic levels.

In accordance with the invention, when the catalyst in the last reforming stage (i.e., in reactor 25) requires regenerating, the deactivated catalyst is replaced by substitute active reforming catalyst without substantially interrupting the reforming process. The substitute active catalyst is disposed in a substitute or redundant reactor 40, and the amount of substitute active catalyst therein may be less than, the same as or more than the amount in the reactor 25, but is preferable about the same.

The reactor 40 may be brought on stream in the naphtha-reforming operation in the following manner:-

Firstly, the fuel supply to the furnaces 14, 20 and 24 is reduced to reduce their heat outputs, and the naphtha feed to the reforming unit from the storage facility 11 is interrupted. The reactor 25 is taken out of service by closing the valves 43 and 44. Preferably, the valves 63 and 65 are also closed. The substitute reactor 40 is made ready for service by opening valves 61, 41 and 42, and then the supply of naphtha feed from the storage facility is resumed by the operation of suitable pumps and valves (not shown), and the supply of fuel to the furnaces 14, 20 and 24 is increased so that the temperature of the naphtha feed and any hydrogen circulating therewith is progressively increased to naphtha-reforming temperatures. The heated naphtha (and any hydrogen-containing gas) raise the temperature of catalyst in the reactors to naphtha-reforming temperatures, and the reactor 40 then operates in place of reactor 25. The time during which the reforming unit is out of service while the foregoing actions are implemented to substitute the reactor 40 for the reactor 25 is typically about 24 hours, although the actual time may vary depending upon the configuration and layout of the reforming unit, the components involved in the reactor substitutions, and the number of human operatives available. However, this non-service time is considerably shorter than the period usually taken to reactivate the catalyst in a semi-regenerative reforming unit. The latter period is usually in the range of from (approximately) 7 to 14 days, and may be approximately 10 days for a typical, competently-operated unit.

Thus the invention reduces the non-operational time of a reformer unit and thereby increases its profitability.

During the reforming operation using reactor 40 as the last naphtha-reforming stage, the first and intermediate reforming stages (i.e., reactor 18 and 22) are operated at slightly higher temperatures than during corresponding periods of the reforming operation employing the reactor 25 in order to compensate for the coke deposits on the catalysts therein. However, due to the

reactions which occur in the last naphtha-reforming stage, the catalyst in reactor 40 becomes deactivated by coke-deposition more quickly than the other reactors. The operating temperatures of the reactors 18, 22 and 40 are raised by appropriate amounts to compensate for their respective progressive catalyst deactivation by coke deposits and when the operation of reactor 40 has attained the maximum desirable level for economic naphtha-reforming, either the reactor 40 may be substituted by another reactor containing active catalyst, in accordance with the invention, or the naphtha-reforming process may be interrupted for regeneration of the catalyst, in accordance with the invention. In most instances, the latter option will be preferred since less investment in the relatively expensive reforming catalyst is required.

The regeneration part of the process cycle is effected employing the following principal steps. The supply of naphtha from source 11 to the reactors is interrupted by suitable valves (not shown), and naphtha and other combustible materials are removed and are purged from the system using, inter alia, a relatively inert gas, such as a flue gas. The inert purge gas is supplied via conduit 45, and purge gas is circulated to all parts of the system by circulation fans 16 (and 33, if present). The valves 43 and 44 upstream and downstream of the reactor 25 are opened so that purge gas passes through the reactor 25. Valves 65, 41 and 42 are open and valves 61 and 63 are closed for the passage of inert purge gas from the reactor 25 into and via reactor 40.

After the reforming unit has been thoroughly purged, an oxygen-containing gas is passed into the reformer unit from line 47. The oxygen-containing regeneration gas may contain a low concentration (e.g., about 1 v%) of oxygen to avoid and/or prevent physical and/or chemical damage to the reforming catalyst. A suitable regeneration gas is a flue gas from a combustion process.

The regeneration gas is passed into the reactor 18 from line 17 at a suitable temperature to cause removal of carbonaceous material therefrom by oxidation, and then passes via lines 21 and 23 to the reactor 22 for coke removal therein at a suitable temperature. The regeneration gas is then passed via line 26 into reactors 25 and 40 to regenerate the catalyst in both reactors. Used regeneration gas is recovered in line 28, and at least part may be discharged from the unit via line 50, either directly to atmosphere or indirectly via suitable purifiers (not shown). Any remaining regeneration gas is passed via cooler 29, line 51 and valve 52 to line 15, where it mixes with added regeneration gas from line 47.

The regeneration gas may pass via the reactors 25 and 40 in series in any order (i.e., either first via reactor 25 and then via reactor 40, or vice versa). In order to regulate the passage of regeneration gas via the reactors 25 and 40, suitable pipes with valves are provided which interconnect the reactors. These interconnecting pipes include first pipe 60, having at least one valve 61,

which connects the normally-upstream ends of the reactors 25 and 40, a second pipe 62, having at least one valve 63, which interconnects the normally-downstream ends of the reactors 25 and 40, and a by-pass pipe 64 having a valve 65 which provides a connection between the first pipe 60 and the second pipe 62.

During a regeneration operation, valves 43, 44, 41, 42 and 65 are open, and valves 61 and 63 are closed, so that regeneration gas passes first via reactor 25 and then via by-pass pipe 64 into the reactor 40 until carbonaceous deposit has been adequately removed from the catalyst.

The regeneration gas is heated as necessary or desirable, and maintained within a suitable temperature band by cooling. The heating and cooling may be effected by any convenient means, e.g., including any of those already mentioned herein.

When the carbonaceous deposit has been adequately removed from the catalyst in all the reactors by the action of the regeneration gas, the catalyst is reactivated by appropriate reactivation procedures. The reactivation procedure may involve adding chlorine to the catalyst, since the catalyst tends to be stripped of chlorine during regeneration. Chlorine (or a chemical precursor thereof) is, supplied from a source 54 and a conduit 55 into each reactor 18, 22, 25 and 40 via respective open valves 57, 58, 59, 43, 44, 65, 41 and 42, until the catalyst in each reactor attains a desired level of chlorination, as determined by known techniques. Thereafter, the supply of chlorine is interrupted, and excess chlorine is purged by inert gas. The catalyst may similarly be treated with other known activation and/or pre-treating agents until restored to a condition suitable for use in a naphtha-reforming process. Thereupon, the reforming unit is purged with inert gas from line 45 until substantially free of reactive chemical entities and then prepared for a further cycle of reforming operations. The valves 43 and 44 remain open so that reformer effluent from reactor 22 and reheater 24 passes into reactor 25, and valve 63 is opened so that reformer effluent from reactor 25 passes to line 28. The valves 41 and 42 are closed so that the reactor 40 is isolated until required for use as a substitute reactor, and the valve 65 is closed to prevent flow via the by-pass pipe 64.

For preference, valve 61 may be closed. Thereafter, naphtha and hydrogen-containing gas are circulated to the reactors 18, 22 and 25 in a first part of the reforming operation, and then to the reactors 18, 22 and 40 in a second part of the reforming operation (in which the reactor 40 is employed as a substitute for the reactor 25) as described. During this second part of the reforming operation, valves 43, 44, 63 and 65 are closed and valves 61, 41 and 42 are open so that feed material in line 26 passes via reactor 40.

Although the embodiment of the drawing has a single substitute reactor 40, it is within the scope of the invention to employ more than one substitute reactor so that the length of each naphtha-reforming run between

regenerations can be further extended. For the embodiment described, the naphtha-reforming operation employing reactor 25 would operate for from 3 to 12 months (e.g., 7 months), and the naphtha-reforming operation employing the substitute reactor 40 would operate for a further 2 to 12 months (e.g., 5 months), before catalyst regeneration and reactivation would be necessary. The foregoing periods and ranges of periods are illustrative, and not to be regarded as limitative. Thus, the process of the invention enable an existing semi-regenerative naphtha-reforming plant almost to double its operating cycle-length without incurring relatively high capital expenditure.

Claims

1. A catalytic reforming process performed in a reforming unit operated with a constant plural number of on-stream catalyst-containing reaction zones connected in series, wherein feed naphtha is passed into the first (or upstream) reaction zone of the on-stream series of reaction zones in the unit and product naphtha having a higher octane rating than the feed naphtha is recovered from the last (or downstream) zone of the on-stream series of reaction zones in the unit, the process comprising, in sequence, the steps of:

(a) passing naphtha into and through the on-stream series of reaction zones of the unit and progressively increasing the temperature of at least the last zone of the on-stream series of zones to maintain the octane rating of the product naphtha at least at a given value until the last on-stream reaction zone of the series attains a specified maximum operating temperature corresponding with a specified degree of deactivation of the catalyst therein;

(b) substituting a different reaction zone containing active reforming catalyst in place of the previous said last on-stream reaction zone of the series in step (a) to maintain a constant number of series-connected reaction zones in the unit, the said previous last reaction zone being maintained off-stream;

(c) continuing the reforming process by passing feed naphtha through the on-stream series-connected reaction zones of the unit without regenerating/reactivating the catalyst in the said previous last reaction zone, and recovering a naphtha product having at least the given octane rating from the last on-stream reaction zone of the series;

(d) progressively raising the temperature of at

least the last reaction zone of the said on-stream series of reaction zones to maintain at least the given octane rating of the product naphtha until the last on-stream reaction zone of the series attains a given maximum operating temperature;

(e) optionally repeating steps (b), (c) and (d), employing a different substitute reaction zone for each step (b);

(f) interrupting the passage of naphtha into and through all the series-connected reaction zones of the unit, and regenerating catalyst (by in situ and/or ex situ regeneration) during the interruption in all the reaction zones employed for reforming in steps (a) to (e); and

(g) optionally repeating steps (a) to (f).

2. The process of claim 1 wherein the amount of catalyst in the last zone of the series in the unit comprises from 50 to 90 weight percent of the total catalyst in the unit.
3. The process of claim 1 or claim 2 wherein the first reaction zone of the series in the unit contains from 5 to 20 weight percent of the total catalyst in the unit.
4. The process of any one of claims 1 to 3 wherein in step (a), the temperature of the first zone is progressively raised to maintain the octane rating of the naphtha product.
5. The process of any one of claims 1 to 4 wherein the unit comprises at least three on-stream reaction zones connected in series.
6. The process of any one of claims 1 to 5 wherein in step (a), the temperature of other reaction zone(s) between the first and last zones is/are progressively raised to maintain the octane rating of the naphtha product.
7. The process of claim 5 or claim 6 wherein the amount of catalyst contained in the on-stream reaction zone(s) connected between the first and last zones of the series is in a range of from 5 to 45 weight percent of the total catalyst in the on-stream zones of the unit.
8. The process of any one of claims 1 to 7 wherein step (f) is effected by in situ regeneration and reactivation of catalyst in all the reaction zones which have been used for naphtha reforming in the unit, the reaction zones, including used and deactivated reaction zone(s), being connected in series to form part of the unit for step (f).

9. The process of claim 8 wherein, following the regeneration and reactivation, the regenerated/reactivated spare reaction zone(s) is/are disconnected from the unit, and step (a) is started.

Patentansprüche

1. Katalytisches Reformierverfahren, das in einer Reformieranlage durchgeführt wird, die mit einer konstanten Mehrzahl im Betrieb befindlicher, katalysatorhaltiger, in Reihe verbundener Reaktionszonen arbeitet, wobei Einsatznaphtha in die erste (oder stromaufwärts liegende) Reaktionszone der im Betrieb befindlichen Reihe von Reaktionszonen in der Anlage geleitet wird und Produktnaphtha mit einem höheren Octanzahlwert als das Einsatznaphtha aus der letzten (oder stromabwärts liegenden) Zone der im Betrieb befindlichen Reihe von Reaktionszonen in der Anlage gewonnen wird, wobei das Verfahren in Abfolge die Stufen umfaßt, in denen

(a) Naphtha in und durch die im Betrieb befindliche Reihe von Reaktionszonen der Anlage geleitet wird und fortlaufend die Temperatur von mindestens der letzten Zone der im Betrieb befindlichen Reihe von Zonen erhöht wird, um den Octanzahlwert des Produktnaphthas mindestens auf einem gegebenen Wert zu halten, bis die letzte im Betrieb befindliche Reaktionszone der Reihe eine spezifizierte Maximalarbeitstemperatur erreicht, die einem spezifizierten Desaktivierungsgrad des darin enthaltenen Katalysators entspricht,

(b) eine andere Reaktionszone, die aktiven Reformierkatalysator enthält, die Stelle der vorhergehenden letzten im Betrieb befindlichen Reaktionszone der Reihe in Stufe (a) einnimmt, um eine konstante Anzahl von in Reihe verbundenen Reaktionszonen in der Anlage aufrechtzuerhalten, wobei die vorhergehende letzte Reaktionszone außer Betrieb gehalten wird,

(c) das Reformierverfahren fortgesetzt wird, indem Einsatznaphtha durch die im Betrieb befindlichen, in Reihe verbundenen Reaktionszonen der Anlage geleitet wird, ohne den Katalysator in der vorhergehenden letzten Reaktionszone zu regenerieren/reaktivieren, und ein Naphthaprodukt mit mindestens dem vorgegebenen Octanzahlwert aus der letzten im Betrieb befindlichen Reaktionszone der Reihe gewonnen wird,

(d) die Temperatur von mindestens der letzten Reaktionszone der im Betrieb befindlichen Reihe von Reaktionszonen fortlaufend erhöht wird, um mindestens den vorgegebenen Octanzahlwert des Produktnaphthas aufrechtzuerhalten, bis die letzte im Betrieb befindliche Reaktions-

- zone der Reihe eine vorgegebene Maximalarbeitstemperatur erreicht,
 (e) gegebenenfalls die Stufen (b), (c) und (d) wiederholt werden, wobei für jede Stufe (b) eine andere Austauschreaktionszone verwendet wird,
 (f) das Leiten von Naphtha in und durch alle in Reihe verbundenen Reaktionszonen der Anlage unterbrochen wird und Katalysator (durch in situ und/oder ex situ erfolgende Regenerierung) während der Unterbrechung in allen zur Reformierung in den Stufen (a) bis (e) verwendeten Reaktionszonen regeneriert wird, und
 (g) gegebenenfalls die Stufen (a) bis (f) wiederholt werden.
2. Verfahren nach Anspruch 1, bei dem die Menge an Katalysator in der letzten Zone der Reihe in der Anlage 50 bis 90 Gew.% des gesamten Katalysators in der Anlage umfaßt.
 3. Verfahren nach Anspruch 1 oder Anspruch 2, bei dem die erste Reaktionszone der Reihe in der Anlage 5 bis 20 Gew.% des gesamten Katalysators in der Anlage enthält.
 4. Verfahren nach einem der Ansprüche 1 bis 3, bei dem in Stufe (a) die Temperatur der ersten Zone fortlaufend erhöht wird, um den Octanzahlwert des Naphthaprodukts aufrechtzuerhalten.
 5. Verfahren nach einem der Ansprüche 1 bis 4, bei dem die Anlage mindestens drei im Betrieb befindliche, in Reihe verbundene Reaktionszonen umfaßt.
 6. Verfahren nach einem der Ansprüche 1 bis 5, bei dem in Stufe (a) die Temperatur der anderen Reaktionszone(n) zwischen der ersten und der letzten Zone fortlaufend erhöht wird, um den Octanzahlwert des Naphthaprodukts aufrechtzuerhalten.
 7. Verfahren nach Anspruch 5 oder Anspruch 6, bei dem die Menge an Katalysator, die in der bzw. den im Betrieb befindlichen Zone(n) enthalten ist, die zwischen der ersten und der letzten der in Reihe verbundenen Zonen liegen, im Bereich von 5 bis 45 Gew.% des gesamten Katalysators in den im Betrieb befindlichen Zonen der Anlage liegt.
 8. Verfahren nach einem der Ansprüche 1 bis 7, bei dem Stufe (f) durch in situ erfolgende Regenerierung und Reaktivierung des Katalysators in allen Reaktionszonen, die zur Naphthareformierung in der Anlage verwendet worden sind, bewirkt wird, wobei die Reaktionszonen einschließlich der gebrauchten und desaktivierten Reaktionszone(n) in Reihe verbunden sind, um einen Teil der Anlage für

Stufe (f) zu bilden.

9. Verfahren nach Anspruch 8, bei dem nach der Regenerierung und Reaktivierung die regenerierte/reaktivierte Ersatzreaktionszone bzw. die regenerierten/reaktivierten Ersatzreaktionszonen von der Anlage getrennt wird bzw. werden und mit Stufe (a) begonnen wird.

Revendications

1. Procédé de reformage catalytique effectué dans une unité de reformage opérant avec un nombre multiple constant de zones réactionnelles contenant du catalyseur en service connectées en série, procédé dans lequel un naphta d'alimentation est envoyé dans la première zone réactionnelle (amont) de la série de zones réactionnelles en service de l'unité et le naphta produit, ayant un indice d'octane plus élevé que le naphta d'alimentation, est récupéré dans la dernière zone (aval) de la série de zones réactionnelles en service de l'unité, ledit procédé comprenant les étapes suivantes en séquence :

(a) on fait passer le naphta dans et à travers la série de zones réactionnelles en service de l'unité et on augmente progressivement la température d'au moins la dernière zone de la série de zones en service pour maintenir l'indice d'octane du naphta produit au moins à une valeur donnée jusqu'à ce que la dernière zone réactionnelle en service de la série atteigne une température opérationnelle maximale spécifiée correspondant à un degré spécifié de désactivation du catalyseur qui s'y trouve,

(b) on substitue une zone réactionnelle différente contenant du catalyseur de reformage actif en lieu et place de ladite dernière zone réactionnelle en service de la série dans l'étape (a) afin de maintenir un nombre constant de zones réactionnelles connectées en série dans l'unité, ladite dernière zone réactionnelle précédente étant maintenue hors service,

(c) on continue le procédé de reformage en faisant passer le naphta d'alimentation à travers les zones réactionnelles connectées en série en service de l'unité sans régénérer/reactiver le catalyseur de ladite dernière zone réactionnelle précédente et on récupère le naphta produit ayant au moins l'indice d'octane donné dans la dernière zone réactionnelle en service de la série,

(d) on élève progressivement la température d'au moins la dernière zone réactionnelle de ladite série de zones réactionnelles en service pour maintenir au moins l'indice d'octane du

- naphta produit à la valeur donnée jusqu'à ce que la dernière zone réactionnelle en service de la série atteigne une température opérationnelle maximale donnée,
- (e) on répète facultativement les étapes (b), (c) et (d) en utilisant une différente zone réactionnelle de substitution pour chaque étape (b),
- (f) on interrompt le passage du naphta dans et à travers toutes les zones réactionnelles connectées en série de l'unité et on régénère le catalyseur (par régénération in situ et/ou ex situ) au cours de l'interruption dans toutes les zones réactionnelles utilisées pour le reformage dans les étapes (a) à (e), et
- (g) on répète facultativement les étapes (a) à (f).
2. Procédé selon la revendication 1, dans lequel la quantité de catalyseur dans la dernière zone de la série de l'unité constitue 50 à 90 % en poids de la totalité du catalyseur de l'unité.
3. Procédé selon la revendication 1 ou 2, dans lequel la première zone réactionnelle de la série de l'unité contient 5 à 20 % en poids de la quantité totale de catalyseur de l'unité.
4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel, dans l'étape (a), la température de la première zone est progressivement élevée pour maintenir l'indice d'octane du naphta produit.
5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel l'unité comprend au moins trois zones réactionnelles en service connectées en série.
6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel, dans l'étape (a), la température de la ou des autres zones réactionnelles entre la première et la dernière zones est progressivement élevée pour amintener l'indice d'octane du naphta produit.
7. Procédé selon la revendication 5 ou 6, dans lequel la quantité de catalyseur contenue dans la ou les zones réactionnelles en service connectées entre la première et la dernière zones de la série se situe dans une plage de 5 à 45 % en poids de la totalité du catalyseur dans les zones en service de l'unité.
8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel l'étape (f) est effectuée par régénération et réactivation in situ du catalyseur de toutes les zones réactionnelles qui ont été utilisées pour le reformage du naphta dans l'unité, les zones réactionnelles, y compris la ou les zones réactionnelles utilisées et désactivées, étant connectées en série pour faire partie de l'unité à l'étape (f).
9. Procédé selon la revendication 8, dans lequel, après régération et réactivation, la ou les zones réactionnelles de réserve régénérées/réactivées est/sont déconnectée(s) de l'unité, et l'étape (a) est amorcée.

